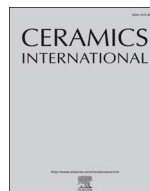




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Influence of Eu doping on the structural, electrical and optical behavior of Barium Zirconium Titanate ceramic

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ABSTRACT

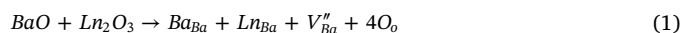
The influence of Eu^{3+} doping on the structural, dielectric and optical behavior of Barium Zirconium Titanate (BZT) with general formula $\text{Ba}_{1-x}\text{Eu}_{2x/3}\text{Zr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ ($x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05$) has been investigated in the present study. The X-ray diffraction (XRD) data show a phase transition from orthorhombic to tetragonal symmetry due to the incorporation of Eu^{3+} ions in $\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ matrix. A secondary phase of $\text{Eu}_2\text{Ti}_2\text{O}_7$ is observed for the composition with $x \geq 0.03$. The Raman spectroscopic study confirms the structural change as observed in XRD, while the Fourier transformation infra red (FT-IR) spectra reveal that Eu^{3+} doping in BZT creates vacancies in the system. The temperature dependent dielectric study shows that the transition temperature and maximum dielectric constant decrease with increase in Eu^{3+} content. It is observed that the dielectric diffuseness increases up to $x \leq 0.02$ followed by a decrease at higher concentrations of Eu^{3+} . The optical behavior of prepared samples is studied through UV–visible spectroscopy, and it is found that the optical band-gap value increases with Eu^{3+} concentration up to 2% and then decreases for higher concentrations ($x > 2\%$).

1. Introduction

Oxide perovskites having general formula ABO_3 are some of the most fascinating and technologically important class of materials in condensed matter research. These materials have found importance in the fabrication of various microelectronic and optoelectronic devices (near ultraviolet and visible range of spectrum) like capacitors, ferroelectric random access memories, sensors, actuators, optoelectronic modulators, etc. [1–10]. Barium Zirconium Titanate ($\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$) is one such system that has attracted research groups all over the world because of its novel electrical properties [11]. The $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ system exhibits high strain, high dielectric constant, low dielectric loss, high voltage resistance, composition dependent Curie temperature and better thermal stability as compared to $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ [12–16].

Doping of rare earth (Re^{3+}) elements (which act as donor) in perovskites is one of the most suitable ways of enhancing the properties of the system [17–23]. Perovskite compounds are the best known inorganic materials for rare earth doping because of their stable crystal structure. Selection of proper dopant plays an important role in improving the dielectric properties of $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ system. It is well reported that up to 4% of molar concentration of rare earth dopant, the

$\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ system exhibits moderate dielectric constant and low dielectric loss [24]. The donors are also used to suppress the growth of grains during sintering, and to obtain low dielectric constant at Curie temperature [25]. The solubility of Re^{3+} ion in $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ system depends on (a) ionic radius of the cation, (b) charge compensation mechanism in case of hetrovalent dopant ion and (c) Ba/Ti concentration ratio. The ions with small ionic radii are substituted into A-site of perovskite, whereas the ions with bigger ionic radii enter the ABO_3 structure at B site. The ions having amphoteric behavior can occupy both cation lattice sites in the ABO_3 structure [20,26]. The charge imbalance created by doping must be compensated by either cation/ionic or electronic vacancies. Ionic vacancies have a negligible effect on conductivity, and the material remains insulating at room temperature (RT), while the electronic vacancies increase the conductivity of the material. The effect of Re^{3+} substitution on Ba-ion can be expressed by Kroger – Vink notation as:



Above equation implies that for every two Ln^{+3} ions positioned in the A-sites, one cationic vacancy V''_{Ba} is necessary for charge neutrality in the perovskite structure. Obviously, the number of vacancies

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increases with increasing Ln^{+3} content. The Eu^{3+} ions doped at A-sites act as a donor, replace Ba^{2+} ions and create A-site vacancies in the system. These lattice vacancies change the order-disorder and local symmetry in the matrix, which influence the optoelectrical and relaxor properties of the system [27].

A perovskite structure is considered to be an ideal matrix for luminescence investigations. Perovskite type compounds are characterized by broad luminescence band at room temperature (RT), and this behavior is attributed to the presence of defects and imperfections in the form of intermediate energy levels in the optical band-gap. Eu^{3+} ion has a specific energy level and a high radiative recombination rate, and this is why, it is preferred as an activator in down conversion phosphors due to the hypersensitive dipole transition $5D_0 \rightarrow 7F_2$ [28].

In past years, $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ system with different doping concentrations of Re^{3+} ions has been widely investigated [20,29–31]. A thorough survey of literature suggests that there was not paid much attention to the normal ferroelectric compositions of BZT perhaps due to lack of commendable dielectric properties. Other than dielectric properties, promising piezoelectric properties in the range of $0.03 \leq x \leq 0.08$ have also been reported by many researchers. Recently, Kalyani et al. [32] have reported that $\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ shows high piezoelectric properties due to the existence of morphotropic phase boundary. This has motivated us to carry out further studies on $\text{BaZr}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.05$) ceramic. However, detailed studies on the electrical and optical properties of $\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ powders with Re^{3+} dopants are yet to be explored. In this context, the main purpose of the present work has been to synthesize and characterize A-site deficient Eu^{3+} doped $\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ (BZT) with different concentration of Eu^{3+} in $(\text{Ba}_{1-x}\text{Eu}_{2x/3})\text{Zr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ system.

2. Synthesis and characterizations

2.1. Synthesis of $\text{Ba}_{1-x}\text{Eu}_{2x/3}\text{Zr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ by solid state reaction method

The $\text{Ba}_{(1-x)}\text{Eu}_{2x/3}\text{Zr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ ($x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05$) ceramics are synthesized by the conventional high temperature solid state reaction route. The starting materials used for this study are BaCO_3 , ZrO_2 , TiO_2 and Eu_2O_3 (all AR grade) provided by Merck India. All the precursors are weighed in the stoichiometric amounts in an electronic balance (Shimadzu ATX 224 single pan analytical balance) followed by mixing and grinding homogeneously in an agate mortar in presence of acetone and distilled water till it becomes slurry. Then, the slurry is mixed until it becomes dry and results in powdered form. The powders are calcined at 1200°C for 4 h at a heating rate of $5^\circ\text{C}/\text{min}$. in a high temperature programmable furnace.

2.2. Experimental techniques

The calcined powders are characterized for phase confirmation through XRD. The samples are examined by means of Panalytical X'pertPro Diffractometer with $\text{Cu-K}\alpha$ ($\lambda = 1.541 \text{ \AA}$) as a radiation source. The X-ray diffraction analysis is carried out in a wide range of 2θ (10° – 90°) at a scanning rate of $2^\circ/\text{min}$. The Raman spectroscopic study is performed in the range of 100 cm^{-1} to 1000 cm^{-1} . For Raman spectroscopic studies, Jobin Yvon Horiba, France make spectrometer (Model T64000) with Argon-Krypton mixed ion gas laser (Spectra Physics Make, USA, Model 2018 RM) is used. The UV–Visible spectra are recorded on Shimadzu make spectrophotometer (Model UV-1800) in diffuse reflection mode. The FT-IR spectra are recorded at RT by the standard KBr pellet technique in a Bruker FTIR spectrophotometer (Model Alpha). The frequency (42 Hz–1 MHz) and temperature (173 K–473 K) dependent dielectric measurements are carried out using a LCR tester (Hioki, Japan) connected to a computer.

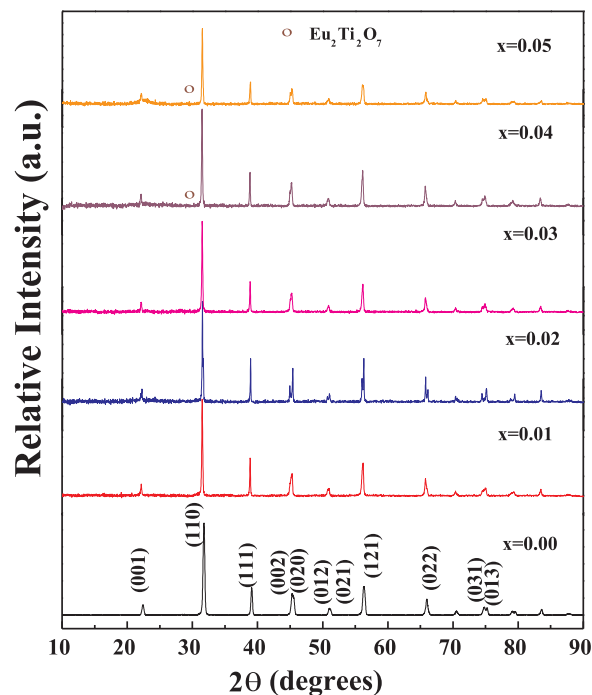


Fig. 1. Room temperature XRD patterns of $\text{Ba}_{1-x}\text{Eu}_{2x/3}\text{Zr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ (with $x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05$) ceramics heat treated at 1200°C for 4 h.

3. Results and discussions

3.1. X-ray diffraction

Fig. 1 shows the XRD patterns of $\text{Ba}_{(1-x)}\text{Eu}_{2x/3}\text{Zr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ ($x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05$) powders calcined at 1200°C for 4 h. Sharp and intense peaks in all the patterns indicate the presence of long range crystallinity in the sample. The majority of reflections are in good agreement with the reported perovskite phase. For $x \leq 2\%$ of BZT: Eu ceramics, no deleterious peak is observed but, for $x > 2\%$, a very small peak due to secondary phase is observed. This small peak of secondary phase is observed in the left of the most intense peak (nearing 31.5°) and is attributed to the formation of $\text{Eu}_2\text{Ti}_2\text{O}_7$. Thus, $x = 0.03$ is the critical point for the solubility of Eu^{3+} ions in BZT, which is supported by similar type of results on Eu^{3+} doped BaTiO_3 [33]. After a thorough analysis, it is concluded that the undoped BZT has orthorhombic structure, while Eu^{3+} doped BZT samples possesses tetragonal perovskite structure at RT. In order to determine various cell parameters, the XRD peaks are analyzed using X'pert high score plus software. The cell parameters for the pure and Eu^{3+} doped samples are enlisted in Table 1. From the table, it can be noticed that the lattice parameters and the unit cell volume decrease with the increase in RE^{3+} concentration. The reason for this decrease in volume and cell parameters is attributed to the smaller ionic radius of Eu^{3+} ions (1.31 \AA) as compared to the ionic radius of Ba^{2+} ions (1.6 \AA).

3.2. Raman spectroscopy

Raman spectroscopy is a technique that uses vibrational modes (Raman active modes) to determine the local structural distortions. The RT Raman spectra of pure and Eu^{3+} doped BZT ceramics studied in the range of 100 cm^{-1} to 1000 cm^{-1} are presented in Fig. 2. As reported earlier [31], the different Raman active modes involved in the spectra are due the deviation from ideal perovskite structure (cubic). Mode ($A_1(\text{TO}_1)$) at 110 cm^{-1} represents distorted octahedral clusters in Eu doped BZT. Raman active mode ($A_1(\text{TO}_2)$) at 184 cm^{-1} is due to the presence of non-polar ZrO_6 clusters in the matrix. A sharp band [B_1, E

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